



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C03C 1/00, 1/02, 3/087, 4/02, 4/08	A1	(11) International Publication Number: WO 99/29634 (43) International Publication Date: 17 June 1999 (17.06.99)
(21) International Application Number: PCT/GB98/03268 (22) International Filing Date: 3 November 1998 (03.11.98) (30) Priority Data: 08/988,481 10 December 1997 (10.12.97) US (71) Applicant (for all designated States except GB): FORD MOTOR COMPANY [US/US]; The American Road, Dearborn, MI 48124 (US). (71) Applicant (for GB only): FORD MOTOR COMPANY LIMITED [GB/GB]; Eagle Way, Brentwood, Essex CM13 3BW (GB). (72) Inventors: JONES, James, Victor; 5255 Snowden Drive, Toledo, OH 43623 (US). BOULOS, Edward, Nashed; 4395 Stonehenge Court, Troy, MI 48098 (US). (74) Agent: MESSULAM, Alec, Moses; A. Messulam & Co., 24 Broadway, Leigh on Sea, Essex SS9 1BN (GB).		(81) Designated States: CA, CN, HU, KR, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: NITRATE/NITRITE-FREE MANUFACTURING OF GLASS WITH SELENIUM (57) Abstract The invention is a method of retaining selenium in a glass containing selenium by including a manganese compound but excluding nitrates or nitrites routinely used in the industry to retain selenium. Particularly, a preferred embodiment involves manufacturing a grey soda-lime-silica glass composition including selenium as a colorant, the components of the grey soda-lime-silica glass have colorants consisting essentially of: greater than 0.9 to 1.9 wt.% total iron oxide as Fe ₂ O ₃ ; 0.10 to 1.00 wt.% manganese compound as MnO ₂ ; 0.0010 to 0.0060 wt.% selenium as Se; 0.002 to 0.025 wt.% cobalt oxide as Co, and 0 to 1.0 wt.% titanium oxide as TiO ₂ which are combined and melted to make the glass composition. The glass composition has at 4.0 mm. thickness: 10 to 55 % light transmittance using Illuminant A, less than 25 % ultra violet transmittance, and less than 50 % infrared transmittance.		

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NITRATE/NITRITE-FREE MANUFACTURING OF GLASS WITH SELENIUM

The invention is directed to a method of manufacturing a glass composition which contains selenium with manganese compound for selenium retention and without the use of
5 nitrate or nitrite. Preferably it includes a reductant like anthracite coal. The glass is a soda-lime-silica glass whose colorants consist essentially of iron oxide, selenium, manganese oxide, cobalt oxide, and optionally titanium
10 oxide.

Many patents including selenium as a colorant have included sodium nitrate or potassium nitrate in the batch mixture to help improve the retention of selenium in the final product or for other purposes. For example, US patents
15 3,296,004; 4,101,705; 4,104,076; and 4,190,452 all disclose bronze glass compositions using selenium together with sodium or potassium nitrates as components of their batches. US patent 4,104,076 also teaches adding selenium and nitrates to the batch to make a grey glass composition as
20 well as a bronze glass composition. US patent 5,070,048 teaches a blue coloured glass product using selenium together with sodium nitrate in the batch mixture. US patents 4,339,541; 4,873,206; 5,023,210; 5,308,805; 5,346,867; 5,411,922; and 5,521,128 are all patents which
25 teach using sodium or potassium nitrate in the batch when selenium is used as a colorant to make grey glass products. Hence, as seen from the above, it is extremely common in the glass making industry to include nitrates when using selenium as a colorant.

30 It is disclosed in US Patent 5,346,867 (Jones '867) a grey glass whose colorants consist essentially of iron oxide, cobalt, selenium and manganese oxide and optionally titanium oxide, the manganese oxide providing selenium retention during processing. Batch materials disclosed
35 therein include sodium and/or potassium nitrate to maintain oxidising conditions early in the melting process which aids in selenium retention. The process for retarding

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volatilisation of the selenium using a manganese containing compound along with the selenium during melt processing, which includes sodium nitrate as a batch component, is claimed in US patent 5,521,128 (Jones et. al '128), a
5 divisional of the '867 patent mentioned above.

One of the disadvantages of using nitrates or nitrites in batch processing is that they can generate environmentally undesirable nitrogen oxide emissions. In addition, we have found that when sodium nitrate is used in
10 the batch, the amount of sodium sulphate (a fining agent) must be lowered which may adversely affect the fining action of sodium sulphate. Otherwise, the retention of selenium would be adversely impacted.

It has unexpectedly found that the manganese compound,
15 e.g., used in the grey glass of Jones '867 to retain selenium, also has sufficient oxidising ability which allows nitrates and nitrites to be avoided throughout the manufacturing process of the selenium containing glass, contrary to what was formerly believed. This also allows the
20 amount of sodium sulphate to be desirably increased over that which would normally be used when nitrates are included in the batch materials, which improves the fining action of the sulphates without negatively impacting the selenium retention. Hence, the present invention nitrate/nitrite-
25 free manufacturing process provides a unique way to make a selenium containing glass, such as the '867 Jones et al. grey glass, in a more environmentally friendly way while retaining selenium retention and in a way that overcomes problems which might develop based on the impact of using
30 nitrates with sulphates.

In US patent application Serial No. 08/691,958 filed August 5, 1996 and entitled "Reduction of Nickel Sulphide Stones In Glass", also having common inventorship and ownership with the present invention, a method is disclosed
35 which involves using a manganese compound to prevent the formation of nickel sulphide stones by encouraging an oxidising environment in the glass melt.

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The present invention is an improved method for manufacturing a selenium containing glass, such as the particular soda-lime-silica grey glass of 'Jones 867, without including nitrates or nitrites in the glass batch during molten glass formation. And while excluding nitrates/nitrites, the method is able to maintain selenium retention as with nitrates or nitrates commonly included therein.

One preferred method is directed to manufacturing the grey composition of '867 Jones which comprises by weight: 68 to 75% SiO_2 , 10 to 18% Na_2O , 5 to 15% CaO , 0 to 10% MgO , 0 to 5% Al_2O_3 , and 0 to 5% K_2O , where $\text{CaO} + \text{MgO}$ is 6 to 15% and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ is 10 to 20%; and colorants consisting essentially of: 0.9 to 1.9 wt. % total iron oxide as Fe_2O_3 , 0.10 to 1.0 wt. % manganese oxide as MnO_2 ; 0.002 to 0.025 wt. % cobalt oxide as Co , and 0.0010 to 0.0060 wt. % selenium as Se , and 0 to 1.0 wt. % titanium oxide as TiO_2 . The glass may also include tramp materials which sometimes enter the glass with raw materials or as a result of changeover of one glass composition to another in a glass furnace. For example, this would include up to about 0.005 wt. % nickel oxide as NiO .

The grey glass products made according to this preferred embodiment of the invention have the following spectral properties at 4.0 mm. thickness: 10 to 55 % light transmittance using Illuminant A (LTA) and less than 25 % ultra violet (UV) transmittance measured over the range of 280 to 400 nanometers and less than 50 % infra red (IR) transmittance measured over the range of 720 to 2120 nanometers.

Further, this grey glass considered at a 4.0 mm. thickness preferably has the following spectral properties: 470-590 dominant wavelength and less than 5.5 % purity of excitation.

The method comprises including a manganese compound while excluding nitrates or nitrites like sodium nitrate from the glass batch along with the selenium to retain

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selenium during melt processing. In order to maintain the same level of selenium retention with only manganese compound as would be retained with manganese compound and nitrate/nitrite, the level of manganese compound is
5 increased in the batch components. That is, an amount of manganese compound needs to be added to replace the amount of nitrate/nitrate excluded. Excluding nitrates/nitrites from the manufacturing process of a glass composition which contains selenium while using manganese compound solely to
10 retain selenium is contrary to what one would expect from the teachings in the patent literature.

Advantageously, it has unexpectedly found that the addition of a manganese compound alone, i.e., without any nitrate/nitrite compounds, to the glass batch to retain the
15 selenium such as in the grey glass (Jones '867 and '128) is sufficient to retain the oxidising conditions even at the beginning of melt processing so that no nitrates nor nitrites are necessary. That is, the manganese oxide acts in the glass batch to sufficiently shift the conditions of the
20 glass batch toward oxidising so that the selenium is retained without the use of the nitrates/nitrites, reducing undesirable nitrogen oxide emissions.

In addition, excluding nitrates/nitrites from batch processing of a glass containing selenium advantageously
25 allows more sodium sulphate to be included in the melt for improved fining action in the glass batch during manufacturing.

The invention is an improved way of manufacturing a glass containing selenium to retain selenium without the use
30 of nitrates or nitrites. An example of such method will be explained herein with reference to a preferred embodiment method, i.e., based on an improved method of manufacturing the grey glass of US patent 5,346,867 to Jones et al. disclosed above, which reference is hereby expressly
35 incorporated by reference in this document for all of its teachings. However, this discussion of the improved method for retaining selenium based on the grey glass is meant to

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apply to other glasses containing selenium as well. This improved method thus involves manufacturing, according to a preferred embodiment, the '867 grey glass without any nitrates or nitrites commonly used in manufacturing glass having selenium as a colorant.

Since selenium is easily vaporised from a glass melt, as discussed above, many patents disclose that when selenium is included as a colorant, it was thought necessary to include nitrates or nitrites like sodium nitrate in the glass melt for retaining selenium. It was disclosed in the '867 and '128 patents that sodium and/or potassium nitrate are used in glass batches of the invention to maintain oxidising conditions early in the melting process which aids in selenium retention. Manganese oxide was included to improve the selenium retention.

The grey glass made according to the preferred improved method is a soda-lime-silica glass, and is useful particularly in the automotive and architectural industries. It is conveniently made by the float glass process. The base glass composition of the grey glass and other glasses used in the automotive or architectural industry is generally characterised by the following composition shown in Table I, the amounts of the components being based on a weight percentage of the total glass composition:

TABLE I

Base Glass Components	Weight %
SiO ₂	68 to 75
Al ₂ O ₃	0 to 5
CaO	5 to 15
MgO	0 to 10
Na ₂ O	10 to 18
K ₂ O	0 to 5

The improved method of this invention is not limited, however, to such soda-lime-silica glasses or the particular grey soda-lime-silica glass discussed in detail herein (the

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'867 Jones et al. glass) as would be apparent to one skilled in the art in view of the present disclosure. Rather, the disclosed improved manufacturing method for retaining selenium may find use in the manufacture of any selenium containing glass to retain the selenium with manganese compounds and without the use of nitrates/nitrites. Generally, in forming such selenium containing glasses according to the present invention improved selenium retention method, raw material components would most generally comprise components like sand, soda ash, dolomite, limestone, salt cake, rouge (for iron oxide colorant), a manganese containing compound, and selenium compound. The amounts and the particular materials employed would depend, however, on the particular glass being produced and selection would be within the skill of one in the art in view of the present disclosure.

The grey glass composition manufactured by the improved method according to one preferred embodiment of the present invention without the use of nitrates/nitrites employs the basic soda-lime-silica glass composition of Table I wherein, additionally, $\text{CaO} + \text{MgO}$ is 6 to 15% and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ is 10 to 20%. In addition, the colouring components of the grey glass composition consist essentially of: 0.9 to 1.9 wt. % total iron oxide as Fe_2O_3 , 0.10 to 1.0 wt. % manganese oxide as MnO_2 , 0.002 to 0.025 wt. % cobalt oxide as Co, and 0.0010 to 0.0060 wt. % selenium as Se, and 0 to 1.0 wt. % titanium oxide as TiO_2 . The glass may also include tramp materials which sometimes enter the glass with raw materials or as a result of changeover of one glass composition to another in a glass furnace. For example, this would include up to about 0.005 wt. % nickel oxide as NiO.

Grey glass products made according to embodiments of invention method have the following spectral properties at 4.0 mm. thickness: 10 to 55 % light transmittance using Illuminant A (LTA) and less than 25 % ultra violet (UV) transmittance measured over the range of 280 to 400 nanometers and less than 50 % infra red (IR) transmittance

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measured over the range of 720 to 2120 nanometers. Further, the grey glass considered at a 4.0 mm. thickness preferably has the following spectral properties: 470 - 590 dominant wavelength and less than 5.5 % purity of excitation.

5 As disclosed in the '867 patent, as it would be known in the art, melting and refining aids are routinely included in glass manufacture and may also be used herein. One refining aid generally used to remove bubbles from the glass is sodium sulphate which results in SO_3 in the glass.
10 Preferably SO_3 is present in the glass composition at 0.10 to 0.30 wt. %, more preferably 0.14 to 0.25 wt.%.

In the improved nitrate/nitrite-free selenium retention method of the present invention, a manganese compound is included to retain selenium since it acts as an oxidiser and
15 one form of manganese oxide absorbs in the same area as selenium colorant so that it can desirably be used to replace a portion of the selenium in providing the glass colour, e.g., the grey colour the Jones '867 glass. The manganese compound is essential to the present invention
20 improved method to retain selenium without the use of nitrates or nitrites, and desirably as discussed above, since this colorant absorbs in the same area as selenium, is able to replace a portion of the selenium as colorant.

The manganese compound is employed in the invention
25 method to provide in the glass an amount of 0.10 to 1.0 wt. % manganese oxide based on MnO_2 , more preferably being 0.15 to 0.8 wt. %, most preferably being 0.15 or 0.20 to 0.60 MnO_2 . This manganese compound colorant can be added to the batch glass components in a variety of forms, for example,
30 but not limited to, MnO_2 , Mn_3O_4 , MnO , MnCO_3 , MnSO_4 , MnF_2 , MnCl_2 , etc. Preferably it is most desirable to use the manganese oxide or manganese carbonate compounds in the batch. As would be appreciated, a mixture of such compounds may also be employed. In the glass composition,
35 this colorant is generally present in the Mn^{+2} and Mn^{+3} state, although it may additionally be present in other states such as Mn^{+4} . As discussed herein, selenium is

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expensive and easily volatilised from the glass melt. Manganese oxide is inexpensive and not subject to such volatility so that it is optimal as a colorant in the present grey glass composition.

5 The manganese colorant has oxidising ability so that when it is added to a glass containing iron oxide, as contained in almost all glass, it is able to shift the redox equilibrium of the iron oxide toward its oxidised form, Fe_2O_3 . As disclosed above, we have found that the use
10 of the manganese oxide colorant, which additionally provides oxidising benefits, allows the elimination of nitrates or nitrites, e.g., commonly used sodium nitrate, as a raw material component in the present invention manufacture of a glass, such as the grey glass. And still, selenium
15 retention is essentially able to maintained as when nitrates/nitrites are included as discussed above. This was unexpected and highly commercially desirable. In general, when selenium is added to a batch as a colorant in prior teachings in the patent literature, sodium nitrate is
20 included in an amount of 5 to 20 pounds per 1000 pounds of sand. One would expect based on calculations, that this amount of nitrate could generate from 2.28 to 9.12 pounds/hour of NO_x emissions per ton of glass produced from a typical mixture of 60 % batch and 40 % cullet. These
25 nitrogen oxide emissions are advantageously eliminated by the improved method of the present invention.

Manganese oxide when added to the glass batch materials as in the embodiment present grey glass invention replaces a portion of the selenium colorant and in the specified
30 amounts retains the selenium by acting as an oxidiser. Generally, one skilled in the art of glass making would not when desiring an oxidising environment as provided by manganese oxide in the grey embodiment glass also add a reducing agent such as anthracite coal. In the instant
35 invention method, however, in the batch the oxidising material is preferably combined with anthracite coal or other like reductants such as graphite, slag from coal fired

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furnaces, blast furnace slag, coke, or the carbonaceous materials. We have found that such preferred use of the anthracite coal enhances the decomposition of sodium sulphate into sulphur trioxide which improves the fining
5 (removal of gaseous inclusions) of the glass batch.

Releasing sulphur trioxide gas into the molten glass helps to coalesce other gases into the bubbles formed and the bubbles rise, expand and burst open at the glass surface releasing the gases therein. This process is well know in
10 the glass industry as fining to improve the quality of the glass. In particular, adding a reductant (e.g., carbocite) to a reducing batch that contains sodium sulphate or calcium sulphate is known to cause the decomposition of the sulphate at lower furnace operating temperatures than without said
15 reductant. We have unexpectedly discovered that during oxidising batch processing, as in the particular embodiment grey glass discussed herein, that we could simultaneously add manganese oxide and a reductant to the batch and maintain the desired oxidising conditions via the manganese
20 oxide in the glass while the fining is improved with the addition of a reductant to the batch. In addition, adding the reductant preferably allows the manufacturing of glass to be carried out at lower temperatures which itself aids in selenium retention. Operating at lower furnace temperatures
25 during melting of the components in the batch furnace also aids in nitrogen oxide reduction from the combustion of the heating gases. Thus several important commercial advantages are obtained by the improved present invention method during production of the glass.

30 The glass composition also includes selenium, in the case of the preferred grey glass in an amount from 0.0010 to 0.0060 wt. % as Se which is an essential ingredient for the grey colour because selenium has a maximum absorption about 500 nanometers and also combines with iron oxide to form an
35 iron-selenium complex with a stronger absorption peak at about 490 nanometers. Manganese oxide in the Mn^{+3} form also has an absorption peak about 490 nanometers so that

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manganese oxide can partially replace selenium in the composition and provide the absorption needed for the grey colour of the glass. Selenium can be added to the glass in a variety of manners including: the elemental metal and in
5 any compound form such as sodium selenite, barium selenite, selenium oxide, sodium selenate, etc.

The following table lists ingredients which are preferably used to form the grey glass compositions according to preferred embodiments of the present invention.

10

TABLE II

BATCH MATERIALS	RANGE MASS (LBS.)
SAND	1000
SODA ASH	290 TO 350
DOLOMITE	215 TO 260
LIMESTONE	70 TO 90
SALT CAKE	6 TO 24
ROUGE (97% Fe_2O_3)	12 TO 26
TITANIUM DIOXIDE	0 TO 7.0
MANGANESE DIOXIDE	1.3 TO 13
COBALT OXIDE (Co_3O_4)	0.25 TO 0.36
SELENIUM	0.20 TO 0.70
CARBOCITE (70% C)	0 TO 1.5
NEPHELINE SYENITE	0 TO 150

The quantities of salt cake and carbocite in Table II
15 represent the largest range that would be used in the batch. Preferably, the improved method for the grey glass uses the following pounds of batch materials: salt cake and carbocite is 8-18 and 0.3-1.0 and most preferably are: 8-12 and 0.4-0.8, respectively per 1000 pounds of sand.

20 In order to demonstrate the advantages of the present invention for the preferred grey glass embodiment manufacturing method, glass was manufactured according to the teachings of patents '128 and '867 by the present inventors as in Example 9 thereof including sodium nitrate.
25 As the run progressed, no further sodium nitrate was added, so that the sodium nitrate was removed from the glass of the batch entirely. Thus in our test, a drop in selenium retention was first observed, and then additional manganese

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oxide was added to compensate for the excluded nitrate, which improved the selenium retention to a level equivalent to or better than with the nitrates. In fact, when the manganese oxide was included in a level 25% by weight higher than the initial manganese oxide amount, it resulted in a slight improvement of selenium retention over that at the beginning of the run when using nitrates. Adding even more manganese compound is expected to improve the selenium retention even further, however, other consideration must be taken into account in the glass manufacture. For example, since including manganese oxide affects the redox ratio of $\text{Fe}^{+2}/\text{Fe}^{+3}$ which can affect the spectral properties, a balance of all of the properties of the glass is considered when selecting the optimal amount of manganese compound to be included for selenium retention as will be apparent to one skilled in the art in view of the present disclosure.

Hence, according to the present invention method, it was found that essentially no additional selenium was released to the furnace atmosphere as the nitrate was no longer added. Hence, selenium retention was maintained in the molten batch even without the use of sodium nitrate. Measurements of NO_x emissions were made during the times when the batch contained sodium nitrate and when the sodium nitrate was removed from the batch, and removing sodium nitrate from the batch led to a 15% reduction of NO_x emissions in the furnace stack (believed due solely to nitrate use elimination in the glass batch).

In subsequent batch mixtures, anthracite coal (commercially called carbocite) was added to the batch as a preferred embodiment of the invention method which led to an improvement in lowering the number of "seeds" (minute undesirable gaseous inclusions) found in the final product due to improved fining of the molten glass. Thus, the present invention method lowered the potential for excess NO_x emissions and improved the quality of the glass product.

Glass compositions including selenium, such as the preferred grey glass composition of Jones '867, made

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according in the present improved invention method can be used for automotive or architectural applications. They are generally made by floating the molten glass on a molten tin bath.

5 Although embodiment of the invention have been described in detail above, it will be appreciated by those skilled in the art that various modifications and alterations can be made to the particular embodiment shown without materially departing from the novel teachings and
10 advantages of the present invention. Accordingly, it is to be understood that all such modifications and alterations are included within the spirit and scope of the present invention as defined by the following claims.

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CLAIMS

1. A method for retarding the volatilisation of selenium used as a colorant in the preparation of a glass composition comprising including a manganese compound colorant along with the selenium in the absence of nitrate or nitrite compounds during the melt processing of the glass composition, the manganese compound being included to provide 0.1 to 1.0 wt. % manganese oxide as MnO_2 weight percent based on the total weight of the glass composition.

2. A method as claimed in claim 1, which further comprises the inclusion of a reductant as a raw material component.

3. A method as claimed in claim 2, wherein said reductant is selected from the group consisting of anthracite coal, blast furnace slag, slag from coal fired furnaces, coke, or graphite, or mixtures thereof.

4. A method as claimed in claim 3, wherein said reductant comprises at least anthracite coal.

5. A method as claimed in claim 3, wherein based on 1000 pounds of sand used to make the base glass composition, batch ingredients further comprise: 6-24 pounds sodium sulphate and 0-1.5 pounds carbocite.

6. A method as claimed in claim 5, wherein based on 1000 pounds of said sand used to make said composition, the batch ingredients comprise: 8-18 pounds sodium sulphate and 0.3-1.0 pounds carbocite.

7. A method as claimed in claim 6, wherein based on 1000 pounds of said sand used to make said composition, the batch ingredients: 8-12 pounds sodium sulphate and 0.4-0.8 pounds carbocite.

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8. A method as claimed in any one of the preceding claims, wherein the amount of manganese compound in the grey glass composition expressed as MnO_2 is 0.15 to 0.8 wt. %.

5

9. A method as claimed in any one of the preceding claims, wherein the glass is a grey, bronze, or blue glass.

10. A method as claimed in claim 9, wherein the dominant wavelength of the grey glass is between 470 and 590 nanometers.

11. A method as claimed in claim 1, wherein the SO_3 is present in the glass composition in an amount between about 0.10 and 0.30 wt. %.

15

12. A method as claimed in any one of the preceding claims, wherein it further comprises floating molten glass made according to the method on a molten tin bath.

20

13. A method as claimed in any one of the preceding claim for making architectural or automotive glass.

14. A method as claimed in claim 8, wherein the amount of manganese compound in the glass composition expressed as MnO_2 is 0.15 to 0.60 wt. %.

25

15. A method for retarding the volatilisation of selenium used as a colorant in preparing a grey glass composition comprising including a manganese containing compound along with the selenium in the absence of nitrate or nitrite compounds during melt processing of the glass composition, said method comprising the steps of: admixing and melting together sand, soda ash, dolomite, limestone, salt cake, rouge, a manganese containing compound, a cobalt containing compound, and selenium, in quantities sufficient to form said grey glass composition having a base glass

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composition comprising by weight: 68 to 75% SiO_2 , 10 to 18% Na_2O , 5 to 15% CaO , 0 to 10% MgO , 0 to 5% Al_2O_3 , and 0 to 5% K_2O , where $\text{CaO} + \text{MgO}$ is 6 to 15% and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ is 10 to 20%; and colorants consisting essentially of: 0.9 to 1.9 wt. % total iron oxide as Fe_2O_3 , 0.1 to 1.0 wt. % manganese oxide as MnO_2 ; 0.002 to 0.025 wt. % cobalt oxide as Co, 0.0010 to 0.0060 wt. % selenium as Se, and 0 to 1.0 wt. % titanium dioxide as TiO_2 all by weight percent based on the total weight of the grey glass composition; the glass having at a 4.0 mm. thickness: 10 to 55% light transmittance using Illuminant A, less than 25 % ultra violet transmittance, and less than 50 % infra red transmittance.

16. A method as claimed in claim 15, wherein based on 1000 pounds of said sand used to make said composition, the batch ingredients comprise: 6-24 pounds sodium sulphate and 0-1.5 pounds carbocite.

17. A method as claimed in claim 16, wherein based on 1000 pounds of said sand used to make said composition, the batch ingredients comprise: 8-18 pounds sodium sulphate and 0.3-1.0 pounds carbocite.

18. A method as claimed in claim 17, wherein based on 1000 pounds of said sand used to make said composition, the batch ingredients comprise: 8-12 pounds sodium sulphate and 0.4-0.8 pounds carbocite.

19. A method as claimed in claim 15, wherein the amount of manganese compound in the grey glass composition expressed as MnO_2 is 0.15 to 0.8 wt. %.

20. A method as claimed in claim 15, wherein the dominant wavelength of the grey glass is between 470 and 590 nanometers.

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21. A method as claimed in claim 15, wherein the SO_3 is present in the grey glass composition in an amount between about 0.10 and 0.30 wt. %.

5 22. A method as claimed in claim 15, wherein it further comprises floating molten glass made according to the method on a molten tin bath.

10 23. A method as claimed in claim 15, wherein said glass has less than 5.5 % purity of excitation.

15 24. A method as claimed in claim 19, wherein the amount of manganese compound in the grey glass composition expressed as MnO_2 is 0.15 to 0.60 et. %.

INTERNATIONAL SEARCH REPORT

In. onal Application No
PCT/GB 98/03268

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C1/00 C03C1/02 C03C3/087 C03C4/02 C03C4/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 99 02461 A (FORD MOTOR CO ; FORD MOTOR CO (US)) 21 January 1999 see the whole document	1-24
P, X	US 5 807 417 A (BOULOS EDWARD NASHED ET AL) 15 September 1998 see column 1, line 9 - line 12 see column 1, line 19 - line 32 see column 2, line 21 - line 25 see column 4, line 15 - line 18 see column 4, line 29 - line 39 see column 6, line 13 - line 19 see column 6, line 44 - line 45 see column 6, line 49 - line 51 see column 8, line 27	1-24
E	& WO 99 02462 A	1-24

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Date of the actual completion of the international search

4 March 1999

Date of mailing of the international search report

16/03/1999

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 98 25863 A (FORD MOTOR CO ; FORD MOTOR CO (US)) 18 June 1998 see page 3, line 16 - line 26 see page 4, line 16 - page 5, line 3 see page 6, line 7 - line 37 see page 9, line 32 - page 10, line 11 see page 12, line 20 - line 21 see page 19, line 3 - line 14 see claim 11; table II ---	1-24
X	US 5 521 128 A (JONES JAMES V ET AL) 28 May 1996 cited in the application see column 1, line 41 - line 47 see column 2, line 25 - line 27 see column 2, line 48 - line 52 see column 4, line 5 - line 8 see claims 1-4, 9, 14; tables ---	1-24
X	US 5 346 867 A (JONES JAMES V ET AL) 13 September 1994 cited in the application see column 1, line 39 - line 45 see column 2, line 48 - line 52 see column 4, line 8 - line 12 see column 4, line 28 - line 32 see claims 1-5, 7-14; tables -----	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

In. International Application No

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9902461	A	21-01-1999	US 5851940 A	22-12-1998
US 5807417	A	15-09-1998	WO 9902462 A	21-01-1999
WO 9825863	A	18-06-1998	US 5776845 A	07-07-1998
			AU 7846498 A	03-07-1998
US 5521128	A	28-05-1996	US 5346867 A	13-09-1994
			CA 2179146 A	22-06-1995
			CN 1137785 A,B	11-12-1996
			DE 69405011 D	18-09-1997
			DE 69405011 T	08-01-1998
			EP 0734358 A	02-10-1996
			ES 2105870 T	16-10-1997
			WO 9516641 A	22-06-1995
			JP 9506584 T	30-06-1997
			US 5521128 A	28-05-1996
US 5346867	A	13-09-1994	CA 2179146 A	22-06-1995
			CN 1137785 A,B	11-12-1996
			DE 69405011 D	18-09-1997
			DE 69405011 T	08-01-1998
			EP 0734358 A	02-10-1996
			ES 2105870 T	16-10-1997
			WO 9516641 A	22-06-1995
			JP 9506584 T	30-06-1997
			US 5521128 A	28-05-1996